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Ground State Energy of Electrons in a Static Point-Ion Lattice

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We investigate the ground state energy of a neutral collection of protons and electrons, under the assumption that in the ground state con-

figuration, static protons occupy the sites of a rigid bravais lattice.  
We use the Higuer-Selts method in conjunction with three postulated

potentials: bare Coulomb, Thomas-Fermi screening, and screening by a uniform background charge. Within these approximations the exact band-  
structure energy and wave function is derived. For each of the three

minima energy and wave function is derived. These three minima ground state energy per proton (relative to isolated electrons and protons) is, respectively, -1.078 Ry, -1.038 Ry,  
and -1.052 Ry. These three minima all fall at a density of about 0.60  
gm/cm<sup>3</sup>, which is thus an approximate lower bound of the density of metallic

hydrogen at its transition pressure.

In the next section we formulate the K-electron, K-proton problem in little labor.  
state energies and accurate wave function may be obtained with relatively  
method (upon which the Higuer-Huntington paper was based) reliable ground  
within the simple, physically appealing framework of the Higuer-Selts  
some of them quite complex. Our purpose in this paper is to show that even  
the intervening years, it has been treated by a variety of techniques.<sup>2-4</sup>  
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we wish to determine the ground state energy of K electrons in the

1. INTRODUCTION  
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thermodynamic limit. We focus entirely on electronic energies, and accordingly take the protons to be fixed at positions  $\{\vec{R}_A\}$ . If the electrons are assigned position and momentum operators  $\{\vec{r}_i\}$  and  $\{\hat{p}_i\}$ , then the Hamiltonian for the system is

$$H = H_{ee} + H_{ep} + H_{pp} \quad (1)$$

where

$$H_{ee} = \sum_i \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \sum_{ij} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \quad (2a)$$

$$H_{pp} = \frac{1}{2} \sum_A \frac{e^2}{|\vec{R}_A - \vec{R}_B|}, \quad (2b)$$

and

$$H_{ep} = - \sum_{iz} \frac{e^2}{|\vec{r}_i - \vec{R}_z|}. \quad (2c)$$

(Here  $m$  is an electron's mass and  $e$  the magnitude of its charge.)

The mean charge density of electrons in this system is  $\rho = -eN/a$ , and the electrostatic energy of a uniform charge distribution with this density is  $\frac{1}{2} \int d\vec{r} d\vec{r}' \frac{\rho^2}{|\vec{r} - \vec{r}'|}$ . The traditional interacting electron gas problem examines the energy of an electron system relative to this term, i.e., the corresponding Hamiltonian is taken to be

$$H_{eg} = \sum_i \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \sum_{ij} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{\rho^2}{|\vec{r} - \vec{r}'|}. \quad (3)$$

The ground state energy of  $H_{eg}$  has been studied extensively:<sup>6,7</sup> when expressed in terms of the linear density parameter  $r_s = (3a/4\pi N)^{1/3} a_0^{-1}$  ( $a_0$  is the Bohr radius), it is approximately

$$E_{eg}^0(r_s) = N \left( \frac{2.21}{r_s^2} - \frac{0.916}{r_s} - 0.115 + 0.031 \ln r_s \right) \text{Ry} \quad (4)$$

where the contributions are the familiar kinetic, exchange and correlation energy terms, the latter being the Nozières-Pines approximation (see below). Note also that in the large system limit, assumed here,  $H_{eg}$  may be written

$$H_{eg} = \sum_i \frac{\hat{p}_i^2}{2m} + \frac{1}{2N} \sum_{k \neq 0} v_c(k) \hat{\rho}_e(k) \hat{\rho}_e(-k) \quad (5)$$

where

$$v_c(k) \approx 4\pi e^2/k^2 \quad (6)$$

and where

$$\hat{\rho}_e(k) = \sum_i e^{i k \cdot \vec{r}_i} \quad (7)$$

is the one-particle density operator for electrons.

If we take  $n(\vec{r})$  as the total charge density of the protons placed in a compensating uniform background of negative charge, i.e.,

$$n(\vec{r}) = \rho + e \sum_A \delta(\vec{r} - \vec{R}_A), \quad (8)$$

then (1) may be regrouped as

$$H = H_{eg} +$$

$$+ \frac{1}{2} \int_0^r d\vec{r} d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} \quad (9a)$$

$$- \sum_k \left( \int \frac{e^2}{|\vec{r}_1 - \vec{R}_k|} + \int \frac{d\vec{r}}{C_k} \frac{pe}{|\vec{r} - \vec{R}_k|} \right). \quad (9c)$$

The term (9b) can now be recognized as the Madelung energy,  $N E_M(r_s, \{\vec{R}_k\})$ , for a static array of ions in a uniform compensating background. As indicated,  $E_M$  depends upon the density and upon the crystal structure of the proton lattice. However, the structural dependence is known to be weak,<sup>8</sup> and  $E_M$  may be accurately estimated using the spherical cell approximation in which each proton is surrounded by a sphere just large enough that the net charge within it vanishes (such a sphere has radius  $r_s^{*0}$ ), and in which the overlap of spheres is ignored. This neutral sphere has electrostatic energy

$$E_M = \int_0^{r_s^{*0}} 4\pi r^2 dr p \left(1 - \left(\frac{r}{r_s^{*0}}\right)^3\right) \frac{e}{r} = -\frac{1.8}{r_s} \text{ Ry.} \quad (10)$$

which accurately approximates the structural result

$$E_M = \frac{1}{2\pi N} \sum_{\vec{k} \neq 0} v_c(\vec{k}) \hat{\rho}_p(\vec{k}) \hat{\rho}_p(-\vec{k}) \quad (11)$$

where

$$\hat{\rho}_p(\vec{k}) = \sum_k e^{i\vec{k} \cdot \vec{R}_k}. \quad (12)$$

(For crystalline lattices  $\hat{\rho}_p(\vec{k}) = N \sum_k \delta_{\vec{k}, \vec{K}_k}$  where  $\{\vec{K}_k\}$  is the set of reciprocal lattice vectors.) Notice that the Madelung part of the Hamiltonian (i.e., 9b) may be rewritten exactly as

$$\frac{1}{2} \frac{N}{C_0} \int d\vec{r} d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{1}{2} \sum_{z,m} \int \frac{d\vec{r}}{C_z} \int \frac{d\vec{r}'}{C_m} \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad (13)$$

where  $C_z$  is the unit cell associated with site  $z$ . The spherical cell approximation therefore calculates the Madelung energy by neglecting the last term of (13) and by replacing  $C_0$  with a sphere of equal volume.

Next we examine (9c), which is the electron-proton interaction energy relative to the interaction energy between protons and a uniform compensating background. We compare two methods for treating this term: first the structural expansion technique, which was applied to a point-ion system (metallic hydrogen) by Hammerberg and Ashcroft,<sup>3</sup> Second, the Wigner-Seitz method which is developed further here. To obtain the structural expansion we first recast (9) into the form

$$H = H_{eg} + NE_M - \frac{1}{2} \sum_{\vec{k} \neq 0} v_c(\vec{k}) \hat{\rho}_e(\vec{k}) \hat{\rho}_p(-\vec{k}), \quad (14)$$

which is valid in the thermodynamic limit. By introducing a coupling constant into the last term we may use a theorem of Pauli<sup>9</sup> to write the ground state energy as

$$\text{NE}^0(r_s, \hat{\mathbf{R}}_k) = \text{NE}_{\text{eg}}^0(r_s) + \text{NE}_H(r_s, \hat{\mathbf{R}}_k) - \frac{1}{a} \sum_{k \neq 0} v_c(k) \hat{\rho}_p(-\hat{k}) \int_0^\infty \langle \lambda | \hat{\rho}_e(\hat{k}) | \lambda \rangle d\lambda \quad (15)$$

where  $|\lambda\rangle$  represents the exact many electron ground state for H at coupling strength  $\lambda$ . Note that (9c) depends on structure through  $\hat{\rho}_p(-\hat{k})$ . The structural expansion calculates  $\langle \lambda | \hat{\rho}_e(\hat{k}) | \lambda \rangle$  by developing it in orders<sup>10</sup> of  $v_c(k) \hat{\rho}_p(\hat{k})$ . The linear term in response theory is

$$\langle \lambda | \hat{\rho}_e(\hat{k}) | \lambda \rangle = x^{(1)}(\hat{k}) \lambda \hat{\rho}_p(\hat{k}) v_c(k) \quad (16)$$

where  $x^{(1)}(\hat{k})$  is the first order polarizability of the interacting electron gas. At this level of approximation

$$E^0 = E_{\text{eg}}^0 + E_H - \frac{1}{2m} \sum_{k \neq 0} v_c^2(k) \hat{\rho}_p(\hat{k}) \hat{\rho}_p(-\hat{k}) x^{(1)}(\hat{k}). \quad (17)$$

Thus, the structural expansion explicitly uses the result (4) of the interacting electron gas problem, and its results may be systematically improved by applying higher orders of response theory.<sup>3</sup>

In contrast, the Wigner-Seitz<sup>1</sup> method involves approximations that are less well defined, and it cannot directly draw upon the standard electron gas result (4). However, it lends itself more readily to direct physical approximation: for example, it calculates approximate one-electron wave functions which are inaccessible via the structural expansion. (The

numerical results of the two methods are, in fact, quite similar.) In the Wigner-Seitz method, one first investigates approximate single-body wave functions  $\psi_k(\hat{r})$  by making an initial assumption (to be improved in Section IV) that when an electron's coordinate is found within the Wigner-Seitz cell of a given proton, the repulsion of the N-1 remaining electrons is exactly canceled by the attraction of the N-1 remaining protons. In this situation an electron is influenced only by its nearest neighbor proton and  $\psi_k(\hat{r})$  then satisfies the single-particle Schrödinger equation

$$(-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r}) \psi_k(\hat{r}) = E_k \psi_k(\hat{r}), \quad (19)$$

where  $\hat{r}$  may now be restricted to a single Wigner-Seitz cell. The boundary condition on this equation is most readily incorporated by invoking the spherical cell approximation, in which<sup>11</sup> the  $\hat{k} = \hat{0}$  wave function is required to be spherically symmetric and satisfies

$$(d\psi_0(r)/dr)_{r_s a_0} = 0. \quad (20)$$

(When  $\hat{k} \neq \hat{0}$ , the appropriate boundary conditions are more complex,<sup>5</sup> but these conditions will not be needed in the following.) Thus the first step in the Wigner-Seitz calculation is to determine the  $\hat{k} = \hat{0}$  "bottom of the band" energy by solving a radially symmetric one-body Schrödinger equation within the spherical unit cell. The total ground state energy for the full Hamiltonian (1) is then estimated using the techniques described in Section III.

## III. TOTAL ENERGY: SPHERICAL CELL APPROXIMATION

If we possessed the  $N$  approximate one-electron wave functions,  $\psi_{\vec{k}}(\vec{r})$ , which are occupied in the ground state, then we could evaluate the exact Hamiltonian (1) in the Slater determinant constructed from these wave functions. The resulting Hartree-Fock-like approximation for the ground state energy is just

$$E_{HF}^0 = \frac{1}{N} \sum_{\vec{k}, s} \int d\vec{r} |\psi_{\vec{k}}(\vec{r})| \left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{|\vec{r} - \vec{r}_0|} \right) \psi_{\vec{k}}(\vec{r}) \quad (21a)$$

$$+ \frac{1}{2N^2} \sum_{\vec{k}, s} \sum_{\vec{k}', s'} \int d\vec{r}_1 d\vec{r}_2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} |\psi_{\vec{k}}(\vec{r}_1)|^2 |\psi_{\vec{k}'}(\vec{r}_2)|^2 \quad (21b)$$

$$- \frac{1}{2N^2} \sum_{\vec{k}, s} \sum_{\vec{k}', s'} \int d\vec{r}_1 d\vec{r}_2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \delta_{s,s'} \psi_{\vec{k}}^*(\vec{r}_1) \psi_{\vec{k}}(\vec{r}_2) \psi_{\vec{k}'}^*(\vec{r}_2) \psi_{\vec{k}'}(\vec{r}_1) \quad (21c)$$

$$+ \frac{1}{2} \sum_{\vec{k}, s} \frac{e^2}{|\vec{r}_0 - \vec{r}_0|}. \quad (21d)$$

where the  $\vec{k}$ 's sums extend over the occupied levels ( $s$  represents the electron spin projection). We assume the wave functions are normalized by

$$\int d\vec{r} |\psi_{\vec{k}}(\vec{r})|^2 = 1 \text{ or } \int_0^r d\vec{r} |\psi_{\vec{k}}(\vec{r})|^2 = 1. \quad (22)$$

Each integral over the volume in (21a-b) may be broken into a sum over lattice sites  $a$  plus an integral over the corresponding Wigner-Seitz cell  $C_a$ . In the spherical cell approximation all of the "cross terms"

involving two different cells can be evaluated exactly, and they conspire to exactly cancel the proton-proton energy (21d). In addition, (19) may be used to simplify (21a), leading to

$$E_{HF}^0(r_s) = \frac{1}{N} \sum_{\vec{k}, s} E_{\vec{k}} \quad (23a)$$

$$+ \frac{1}{N^2} \sum_{\vec{k}, s} \sum_{\vec{k}', s'} \frac{1}{2} \int d\vec{r}_1 d\vec{r}_2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} |\psi_{\vec{k}}(\vec{r}_1)|^2 |\psi_{\vec{k}'}(\vec{r}_2)|^2 \quad (23b)$$

$$- \frac{1}{2N^3} \sum_{\vec{k}, s} \sum_{\vec{k}', s'} \int d\vec{r}_1 d\vec{r}_2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \delta_{s,s'} \psi_{\vec{k}}^*(\vec{r}_1) \psi_{\vec{k}}(\vec{r}_2) \psi_{\vec{k}'}^*(\vec{r}_2) \psi_{\vec{k}'}(\vec{r}_1) \quad (23c)$$

where the sums are understood to be over the occupied levels. We will treat each of the three components in turn.

First, we examine the average single-body energy, (23a). The first term in the sum is just  $E_0$ , the band minimum, which is found by solving the boundary value problem

$$- \frac{\hbar^2}{2m} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) \phi_0(r) - \frac{e^2}{r} \phi_0(r) = E_0 \phi_0(r), \quad (24)$$

$$(d\phi_0/dr)_{r_s a_0} = 0. \quad (25)$$

Following Bardeen,<sup>5</sup> we make the substitutions  $S = r\phi$ ,  $E_b = -E_0/(e^2/2a_0)$  and  $y = 2E_b^{1/2}r/a_0$ . The equation for  $S$  is then Whittaker's equation

$$\frac{d^2\psi}{dy^2} + \left[ \frac{\epsilon_b^{-1/2}}{y} - \frac{1}{4} \right] \psi = 0 \quad (26)$$

which leads to the solution, regular at the origin,

$$\psi_0(y) = Ae^{-y/2} M(1 - \epsilon_b^{-1/2}; 2; y) \quad (27)$$

where  $M(a; b; y)$  is Kummer's confluent hypergeometric function.<sup>12,13</sup>

Application of the boundary condition (25) then leads to the simple nonlinear eigenvalue equation

$$\left( \frac{1}{2} y_s - 1 - \epsilon_b^{-1/2} \right) M(1 - \epsilon_b^{-1/2}; 2; y_s) + \left( 1 + \epsilon_b^{-1/2} \right) M(-\epsilon_b^{-1/2}; 2; y_s) = 0. \quad (28)$$

The binding energy  $\epsilon_b$  is easily found by solving (28) numerically: in the regime of interest Kummer's function may be evaluated to desired accuracy by simply retaining more and more terms of its power series representation. The normalized wave function for  $r_s = 1.5$  is plotted in figure 1.

The wave function (27) has a cusp at the origin, as do all the hydrogen atom wave functions. In fact, all these cusps are identical in that

$$(d(\ln \psi)/dr)_{r=0} = -s_0^{-1}. \quad (29)$$

This cusp condition has recently been proven to apply under very general conditions:<sup>14</sup> it will aid us in later calculations when no exact solution

is available.

We must now find the effect of the potential  $V(r)$  on  $E_0$  when  $k \neq 0$ . These effects are manifested principally in an effective mass  $m^*$ , defined by

$$E_k = E_0 + \frac{\hbar^2 k^2}{2m^*} + O(k^3). \quad (30)$$

(The higher order terms in  $k$  may be ignored because the band is only half filled.) Bardeen<sup>5</sup> has shown that  $m^*$  is given by

$$\frac{n}{m^*} = \frac{4}{3} \left[ (r_s s_0)^3 \left[ \psi_0^2(r) \left( \frac{r}{P} \frac{dP}{dr} - 1 \right) \right]_r \right]_{r=r_s} = r_s s_0 \quad (31)$$

where the function  $P(r)$  is a solution of

$$\frac{d^2P}{dr^2} - \frac{2}{r^2} P + \frac{2n}{\hbar^2} (E_0 - V(r)) P = 0. \quad (32)$$

For a Coulomb potential we may use the variables introduced in (26) to write this equation as

$$\frac{d^2P}{dy^2} + \left[ -\frac{1}{4} + \frac{\epsilon_b^{-1/2}}{y} - \frac{2}{y^2} \right] P = 0, \quad (33)$$

which is once again Whittaker's equation. The  $P(r)$  dependent quantity in (31) is given by

$$\left(\frac{r}{p} \frac{dp}{dr}\right)_{r_s a_0} = \left(\frac{y_s}{2} - \varepsilon_b^{-1/2}\right) + \left(2 + \varepsilon_b^{-1/2}\right) \frac{M(1 - \varepsilon_b^{-1/2}; 4; y_s)}{M(2 - \varepsilon_b^{-1/2}; 4; y_s)}. \quad (34)$$

Once  $m^*$  is thus obtained, we approximate (23a) by

$$\frac{1}{N} \sum_{k,s} E_k = E_0 + \left(\frac{m}{m^*} \frac{2.21}{r_s^2}\right) \text{Ry.} \quad (35)$$

Now we investigate the Hartree energy (23b). The first term in the sum is

$$H_{00} = \frac{e^2}{2} \frac{\int \int dr_1 dr_2 v_0^2(r_1) v_0^2(r_2)}{C_0 C_0 |r_1 - r_2|} = 16e^2 \frac{r_s a_0}{\pi} \int_0^{r_s a_0} dr r v_0^2(r) \int_0^r dr' r'^2 v_0^2(r'). \quad (36)$$

This term can be evaluated using the power series representation for Kummer's function, but convergence is slow enough that this is not practical for  $r_s$  greater than about 3.5. For larger values of  $r_s$  the integral is readily evaluated numerically. The remaining terms in the Hartree sum can also be evaluated, but only with considerable effort. This may be avoided, however, by noting that (36) is the largest term in the Hartree sum. This follows from the observation that the low energy  $k = 0$  wave function is itself much larger near the center of the cell (where potential energy is low) than at its edge, whereas the high energy wave functions are more uniform in amplitude. On the other hand, a lower bound on the sum is necessarily given by the Hartree integral for a flat

wave function, namely

$$16e^2 \frac{r_s a_0}{\pi} \int_0^{r_s a_0} dr r \frac{3}{4\pi(r_s a_0)^3} \int_0^r dr' r'^2 \frac{3}{4\pi(r_s a_0)^3} = \frac{6}{5r_s} \text{Ry.} \quad (37)$$

At  $r_s = 1.5$ , the upper bound (36) is only 5% larger than the lower bound (37). This fortunate numerical coincidence implies that little error is introduced by taking the sum (23b) as the average of the two bounds (36) and (37). This is precisely the approximation that we will employ.

The remaining exchange term (23c) is traditionally difficult to evaluate. Wigner and Huntington<sup>1</sup> argue that it is closely approximated by the uniform interacting electron gas result  $-(0.916/r_s)$  Ry, and we also accept this result.

Finally,  $E_{\text{HF}}$  must be corrected by adding a correlation energy. We will again use a uniform electron gas result, namely the Nozières-Pines<sup>2</sup> interpolation formula  $(-0.115 + 0.031 \ln r_s)$  Ry. Our final approximation for the ground state energy per electron is thus

$$E^0(r_s) = E_0 + \left[\frac{m}{m^*} \frac{2.21}{r_s^2} + \frac{1}{2} (H_{00} + \frac{6}{5r_s}) - \frac{0.916}{r_s} - 0.115 + 0.031 \ln r_s\right] \text{Ry.} \quad (38)$$

where  $H_{00}$  appears in (36). This result is plotted in figure 2: the zero pressure density corresponds to  $r_s = 1.66$ , at which point the cohesive energy (relative to well-separated electrons and protons) is  $-1.078$  Ry. The results are numerically quite close to those of Chakravarty *et al.*<sup>2</sup>, which were obtained using a completely different method.

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Because the Hamiltonian is explicitly spin-independent, the above discussion is readily extended to consider a spin polarized ground state. In this case the kinetic energy term  $2.21/r_s^2$  becomes  $3.51/r_s^2$ , and the exchange term  $-0.916/r_s$  becomes  $-1.154/r_s$ . Otherwise equation (38) is unchanged. These results are also graphed in figure 1: paramagnetic and spin aligned energies are seen to be equal at  $r_s = 3.50$ .

#### IV. SCREENING EFFECTS

In Section III we found approximate single-body wave functions from a Schrödinger equation which ignored electron-electron repulsion. Subsequently, the total energy was obtained by evaluating the exact Hamiltonian in a state constructed from these wave functions. Better wave functions, and more accurate energies, may be obtained by utilizing a screened potential. The Schrödinger equation then becomes (hereafter we use atomic units with  $Ry = a_0 = e^2/2 = 1$ )

$$\left(-\frac{r^2}{r} + U(\vec{r})\right) \psi_k(\vec{r}) = E_k \psi_k(\vec{r}), \quad (39)$$

where  $U(\vec{r})$  is some average potential arising from electron-electron repulsion. We now examine two such screening potentials: first the potential of a negative unit charge uniformly distributed throughout the Wigner-Seitz sphere, namely

$$U_B(\vec{r}) = \frac{1}{r_s^3} (3r_s^2 - r^2). \quad (40)$$

Second, a Thomas-Fermi screening potential

$$U_{TF}(r) = \frac{2}{r} (1 - e^{-k_{TF}r}), \quad k_{TF} = \left(\frac{12}{\pi}\right)^{1/3} \frac{1}{r_s^{1/2}}. \quad (41)$$

For the first case the  $\vec{k} = \vec{0}$  Schrödinger equation can be solved exactly using the power series method. For the second the Schrödinger equation is analyzed variationally.

We begin by noting that the total Hamiltonian (1) can be trivially rewritten as:

$$H = H + \sum_{1,2} U(\vec{r}_1 - \vec{R}_2) - \sum_{1,2} U(\vec{r}_1 - \vec{R}_1), \quad (42)$$

where  $U(\vec{r})$  is now chosen to vanish for  $\vec{r}$  outside the Wigner-Seitz cell. By evaluating this Hamiltonian in a Slater determinant composed of solutions to (39), we find that the Hartree-Fock-like energy (23) is altered only by the addition of the (negative) term

$$-\frac{1}{N} \sum_{k,s} \int_0^{\infty} dr |\psi_k(\vec{r})|^2 U(r). \quad (43)$$

This sum can be estimated (as the Hartree sum was), by averaging the lower bound

$$-4\pi \int_0^{r_s} r^2 dr \langle \psi_0^2(r) U(r) \rangle \quad (44)$$

and the upper bound (obtained using unmodular wave functions in (43))

$$-\frac{4\pi}{3} \int_0^{r_s} r^2 dr U(r). \quad (45)$$

This last expression is equal to

$$-12/(5r_s), \quad (\text{uniform background potential})$$

$$-\frac{6}{r_s^3} \left[ \frac{r_s^2}{2} - \frac{1}{k_{TF}} + e^{-k_{TF}r_s} \left( \frac{r_s}{k_{TF}} + \frac{1}{k_{TF}} \right) \right], \quad (\text{Thomas-Fermi potential}).$$

As with the earlier Hartree sum, the loss of accuracy involved in this bounding procedure is not serious. Note that at  $r_s = 1.5$  the two bounds differ by only 3% (for both potentials).

We will treat the uniform background potential first. The boundary value problem for  $\psi_0(r)$  is then

$$\left[ -\frac{d^2}{dr^2} - \frac{2}{r} \frac{d}{dr} - \frac{2}{r} + \frac{1}{r_s^3} (3r_s^2 - r^2) \right] \psi_0(r) = E_0 \psi_0(r), \quad (46)$$

$$(d\psi_0/dr)_{r_s} = 0. \quad (47)$$

Although (46) is apparently not a "standard" or "named" differential equation, it is easily solved using the method of Frobenius.<sup>15</sup> Only one solution is regular at the origin, and it is

$$\psi_0(r) = \frac{A}{r} S(r) = \frac{A}{r} \sum_{i=0}^{\infty} s_i r^i, \quad (48)$$

where

$$s_0 = 0, \quad s_1 = 1, \quad s_2 = -1, \quad s_3 = (1/6)(2-E_0 + 3/r_s) \\ s_4 = -\frac{1}{1(1-1)} (3s_{1-1} + (E_0 - \frac{3}{r_s}) s_{1-2} + \frac{1}{r_s^2} s_{1-4}), \quad 124 \quad (49)$$

The series for  $S(r)$  converges absolutely and uniformly for all  $r$ , so we may interchange differentiation and summation. Hence boundary condition (47) becomes

$$\sum_{i=1}^{\infty} (i-1) s_i r_s^{i-1} = 0, \quad (50)$$

which leads to an eigenvalue equation for  $E_0$ , and which is easily solved numerically. Notice that the cusp condition (29) is exactly satisfied by wave function (48), despite the use of a non-Coulombic potential (see footnote 8 of reference 14).

The effective mass may be determined from equations (31) and (32), where now  $V(r) = -2/r + U_0(r)$ . The relevant solution of (32) is

$$\Psi(r) = \sum_{l=0}^{\infty} p_l r^l; \quad p_0 = p_1 = 0, p_2 = 1, p_3 = -1/2$$

$$p_1 = \frac{-1}{1(1-1)-2} (2p_{1-1} + (E_0 - \frac{3}{r_s^3})p_{1-2} + \frac{1}{r_s^3} p_{1-4}), \quad l \geq 4 \quad (51)$$

Finally the Hartree, exchange, and correlation energies are treated as they were for a pure Coulomb potential. To the ground state energy formula (38) we must therefore add our estimate for the sum (43). The resulting energy estimate is plotted against  $r_s$  in figure 3. The minimum energy,  $E^0 = -1.052$  Ry, falls at  $r_s = 1.65$ .

The analysis of the Thomas-Fermi potential may be approached using the same power series method. Indeed, we find that (49) is replaced by

$$s_0 = 0, s_1 = 1, s_1 = -\frac{1}{1(1-1)} \left( 2 \sum_{m=0}^{l-1} \frac{(-k_{TF})^{l-m-1}}{(l-m-1)!} s_m + E_0 s_{l-2} \right) \stackrel{l \geq 2}{=} . \quad (52)$$

The cusp condition is again satisfied exactly. However, because  $s_1$  depends upon all the preceding coefficients  $s_0$  to  $s_{l-1}$ , we have not been able to establish that the series actually converges. Numerical evidence indicates that it does, in fact, converge, but only very slowly. For  $r_s$  greater than about 1.2, convergence is slow enough that the exact power series solution is of little help in practical calculations. These are physically important values of  $r_s$ , so a different approach is clearly required.

The variational method proves to be an accurate technique for finding  $E_0$  and  $\psi_0(r)$ . A suitable trial wave function  $\psi_t(r)$  must satisfy the

symmetry condition

$$\psi_t(r_s + \Delta) = \psi_t(r_s - \Delta), \quad (53)$$

in order to assure that the boundary condition (20) is satisfied in such a way that the wave function is smooth at  $r = r_s$ . In addition, it is expected to behave like the 1s hydrogenic wave function near the origin, i.e.,

$$\psi_t(r) = A e^{-r} \text{ for } r \ll r_s. \quad (54)$$

Both of these requirements are satisfied by the choice

$$\psi_t(r) = b_0 \cosh(r-r_s) + \sum_{n=1}^N b_n \sin \frac{(2n-1)\pi r}{2r_s}. \quad (55)$$

This  $\psi_t(r)$  does not automatically satisfy the cusp condition (29). We may therefore adopt either of two variational strategies: 1) vary all chosen parameters in  $\psi_t(r)$  while imposing one constraint (normalization), or 2) increase the variational sum by one term, vary all parameters, and impose two constraints (normalization, and the cusp condition). In either case the variational problem is straightforward and the results are actually quite similar. This technique can easily be checked by using it to recalculate  $E_0(r_s)$  for the Coulomb potential itself. With  $N = 5$  in the sum, the variational and truncated series results differed by only parts per million throughout the range  $0 < r_s < 5$ . The  $r_s = 1.5$  variational

wave function cannot be distinguished from figure 1 because of the width of the tracing pen.

The Hartree integral (36) and the "screening correction" integral (44) are straightforwardly computed from the  $\vec{k} \cdot \vec{v}$  variational wave function. The only remaining obstacle is the effective mass, which can again be found by integrating (32) numerically. Alternatively, the band width (and hence  $m^*$ ) may be calculated from an isotropic two plane wave model appropriate for a spherical Brillouin zone.<sup>16</sup> If  $K$  is the magnitude of the shortest reciprocal lattice vector (so that  $K/2$  is the radius of the first Brillouin zone and  $\frac{4}{3}\pi r_s^3$ ,  $\frac{4}{3}\pi = (K/2)^3 = (2\pi)^3$ ), then in this model the energy  $E(k)$  relative to  $V(\vec{k} = \vec{0})$  is given by

$$E(k) = \frac{E_0(k) + E_0(k-K)}{2} - \left[ \left( \frac{E_0(k) + E_0(k-K)}{2} \right)^2 + V^2(k) \right]^{1/2} \quad (56)$$

where  $E_0(k) = k^2$  and  $V(k)$  is the Fourier transform of the potential. From (56) we find an approximate band width,

$$E_w = E_0(K/2) - |V(K)| - E(0) = \frac{m}{m^*} (K/2)^2. \quad (57)$$

which defines the effective mass  $m^*$ . The results of the two methods are rather similar (the two effective masses differ by 5% at  $r_s' = 1.5$ ). In the following we will use the results of the first method.

The ground state energy of this last model is again plotted in figure 3. The minimum falls at  $r_s = 2.61$ , where  $E^0 = -1.038$  Ry, a value which is in close agreement with the results of Tua and Nahm.<sup>6</sup>

## V. CONCLUSIONS

It is worth emphasizing that the work reported here is not a statistical mechanical calculation. We do not examine all possible states of H and find which is the most probable. Instead we have proceeded from the assumption that the most probable state for the density range of interest is a metallic one in which the protons occupy the sites of a Bravais lattice. The spherical cell approximation obviously eliminates any reference to the choice of Bravais lattice, and also eliminates the possibility that the ground state is some other configuration, such as a lattice with a diatomic basis (which is the experimental structure at zero temperature and atmospheric pressure) or a "liquid" in which the proton disorder is due not to thermal agitation, but to quantum fluctuations.<sup>17</sup> It is thus not surprising that our curves show physically irrelevant negative pressure for  $r_s$  greater than about 1.65. This simply reflects the well-known fact that at these densities the ground state is not a Bravais lattice metal, but is either a molecular solid or a metal in coexistence with such a solid. To complete the equation of state for hydrogen, then, we need to find  $E^0(r_s)$  for a lattice with a diatomic basis,<sup>18</sup> and connect the two curves using a Gibbs tangent construction. Of course, there remains always a possibility that a third configuration, with still lower energy, is the true ground state. Accordingly our calculations do not profess to find the zero temperature equation of state for hydrogen, but rather the ground state energy of electrons in the presence of a putative static Bravais lattice of protons. (The major difference between this model and a plausible picture of metallic hydrogen is the lack of ionic motion.) The results do, however, show that if metallic hydrogen exists in a stable

or metastable state, then it must have a density greater than about 0.60 gm/cm<sup>3</sup> (which corresponds to  $r_s = 1.65$ ).

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13. The normalization constant A can be determined from the result

$$\int_0^{\infty} e^{-\gamma y^2} n^2(a,b,y) dy = \prod_{n=0}^{\infty} \prod_{m=0}^n \frac{(a)_m (a-m)_{n-m} (n+2)_m}{(b)_m (b)_{n-m} m! (n-a)!} [(1-e^{-y_s}) \sum_{k=0}^{n+2} \frac{y_s^{n+2-k}}{(n+2-k)!}]$$

where

$$(a)_n = a(a+1)\dots(a+n-1) \quad n \geq 1$$

$$= 1 \quad n = 0.$$

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FIG. 1. The band minimum wave function  $\psi_0(r)$  at  $r_s = 1.5$ , as given by (27).

FIG. 2. Solid line: The ground state energy  $E^0(r_s)$  calculated from a bare Coulomb potential using (38). Dashed line: a similar result assuming a spin aligned ground state, i.e., one with only one electron allowed in each spatial wave function.

FIG. 3. The ground state energy per proton  $E^0(r_s)$  calculated in the Wigner-Seitz approximation with various one-body potentials. Solid line, Coulomb potential; dashed line, uniform background potential; dotted line, Thomas-Fermi potential. The cross marks the experimentally determined cell radius and ground state energy of solid molecular hydrogen at atmospheric pressure ( $r_s = 3.118$ ,  $E^0 = -1.1648$  Ry.). The inset shows the progression with  $r_s$  of the  $k = 0$  band minimum as determined by (28) for the pure Coulomb potential.

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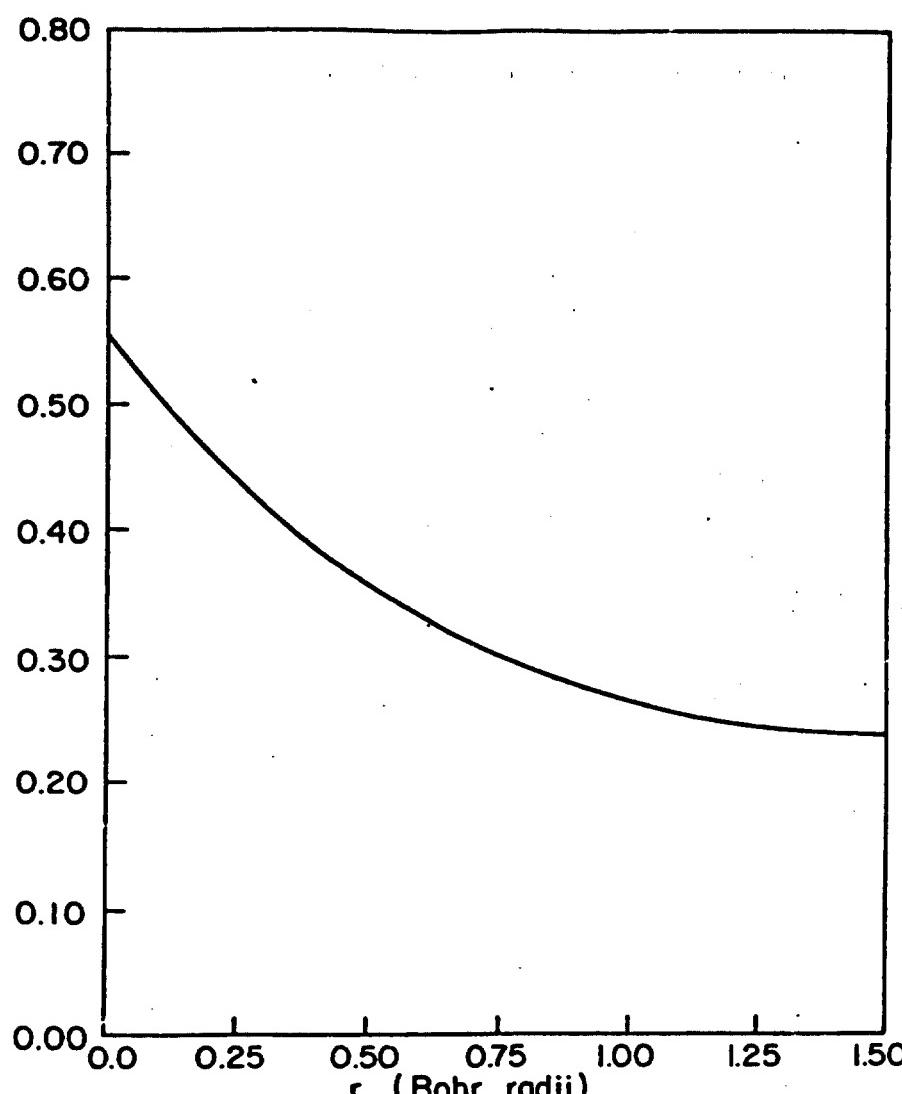


Figure 1

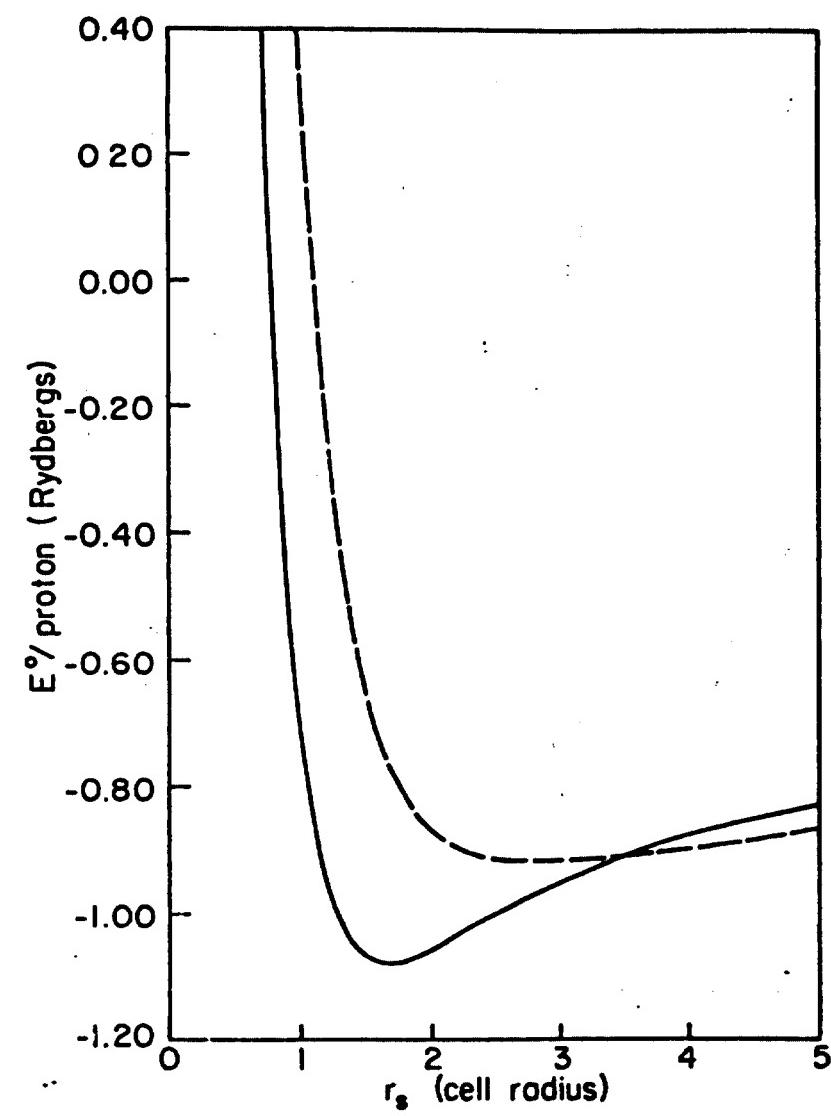


Figure 2

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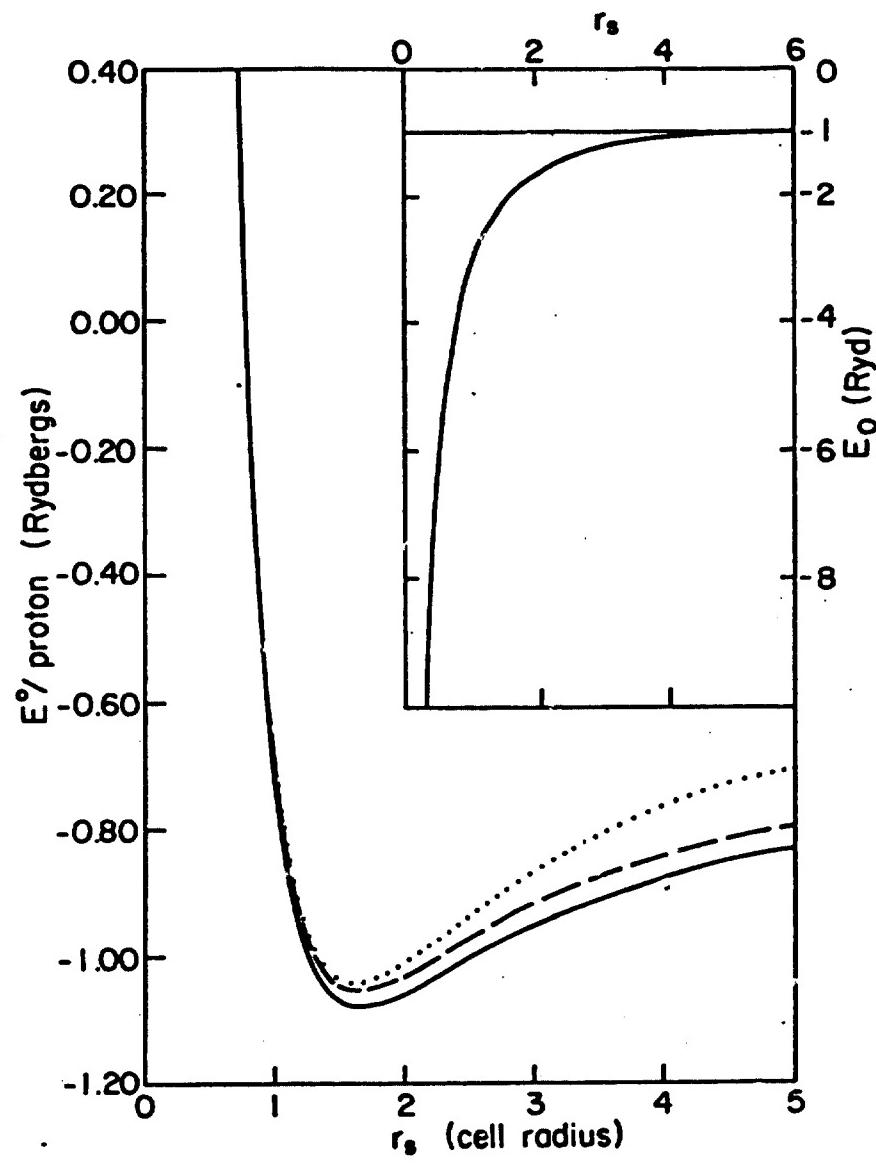


Figure 3